Determination of Total Carbon Dissolved in Aqueous Samples by Inductively Coupled Plasma Atomic Emission Spectrometry

Kenji ISSHIKI

Department of Applied Science, Kochi Women's University, Kochi 780, Japan

ABSTRACT

Total carbon dissolved in aqueous samples is determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Carbon of nonvolatile compounds can be determined with a detection limit of 1.6 mg/L and a reproducibility of 0.60% at 500 mg/L as carbon regardless of their chemical form, by direct aspiration of sample solution. Background interferences originating from the emission of carbon impurities in argon limit the detection capabilities of carbon in samples. Volatile carbon compounds give increasing sensitivity of carbon. The enhancement of sensitivity is attributable to the improvement in introduction efficiency of the analyte into plasma. Application of ICP-AES to direct determination of total carbon in waste water is described.

INTRODUCTION

Emission spectrometry using an atmospheric pressure plasma, such as a microwave induced plasma, an arc or spark discharge plasma, and an inductively coupled plasma (ICP), has been intensively investigated by many researchers as simultaneous multielement determination methods[1]. Among them, an ICP has the following characteristics : the high temperature of the plasma (about 9,000 K[2]) and the long residence time of analyte in the plasma[3] allow all chemical species to be converted into atoms or atomic ions. Thus, inductively coupled plasma atomic emission spectrometry (ICP-AES) is expected to be the most appropriate method for determination of total dissolved elements regardless of their chemical form.

Recently, the capability of ICP-AES for determination of total dissolved elements in aqueous samples has been demonstrated in the determination of germanium[4] and silicon[5]. For carbon, another Group 14 element, ICP-AES has been applied to elemental analysis of gaseous sample[6]~[8]. The present paper is focused on the advantages and disadvantages of ICP-AES in the determination of total carbon (TC) in aqueous samples.

EXPERIMENTAL

Reagent

All chemicals used were of analytical reagent grade. Standard solutions of the carbon compounds were prepared by dissolving dried materials into 0.1 M aqueous hydrochloric acid solution. Distilled deionized water (DDW) was used to prepare the aqueous solutions. Argon

gas supplied to the ICP system was compressed high purity argon (99.998%) in a gas cylinder.

Apparatus

A Shimadzu ICPQ-100 ICP spectrometer equipped with a Shimadzu GE-50A monochromator was used. The specifications of the facilities are shown in Table 1 together with the operational parameters that were optimized by the one-factor-at-a-time method by using an aqueous solution of oxalic acid.

Table 1. The specifications and the operational parameters of the ICP system

RF frequency		27.120 MHz
RF power		1.00 kW
Gas flow rate	Coolant gas (Ar)	12.0 L/min
	Plasma gas (Ar)	0.8 L/min
	Carrier gas (Ar)	1.0 L/min
Sample uptake rate		1.40 mL/min
Sample aspiration		forced by peristaltic pump
Nebulizer		glass, concentric type
Plasma torch		quartz, Fassel type
Optical system	Focal length	50 cm (Czerny-Turner)
	Grating	1200 grooves/mm
	Entrance slit width	10 μm
	Exit slit width	10 μm
Observation height above load coil		12.5 mm
Signal integration time		10.0 s

RESULTS AND DISCUSSION

Background Emission

The intensity and stability of background emission is one of the most important factors that limit the detection capabilities of analyte in emission spectrometry including ICP-AES. Figure 1 shows the background emission spectrum of ICP when DDW is aspirated. It clearly indicates that two sharp emission lines appear on the continuum of the emission. The wavelength of the two lines was measured to be 193.1 nm and 247.9 nm, which were identified to be carbon emission lines at 193.091 nm and 247.856 nm, respectively[9]. The background carbon emission is not due to dissolved carbon dioxide in aqueous samples, bacause DDW in which carbon dioxide was thoroughly removed by bubbling nitrogen in it and boiling it after acidification yielded no change in the background carbon emission.

The emssion profile of the atomic carbon line at 247.856 nm in a plasma flame was determined to clarify the nature of the background carbon emission. The profile of the intensity of the background emission peak and that of the net signal intensity (the intensity increase caused by the introduction of sample) in aspirating samples containing oxalic acid are shown in Figure

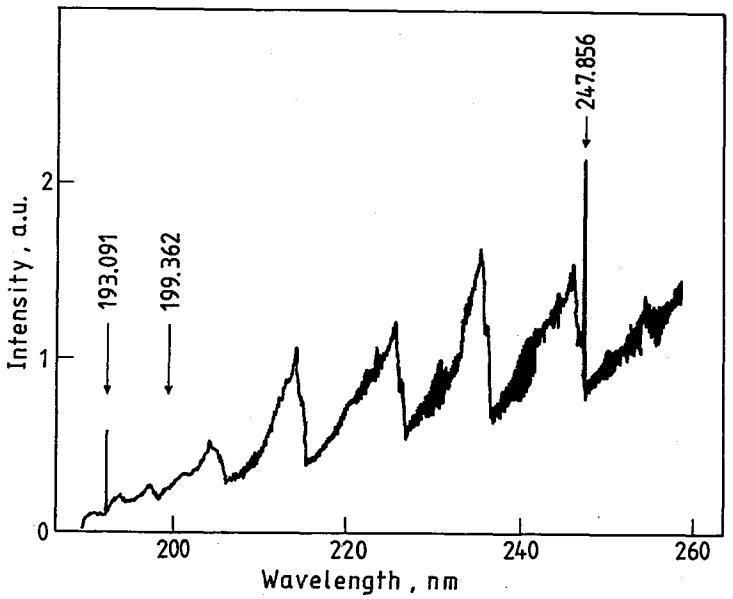

Figure 1. Typical Spectrum of Background Emission.

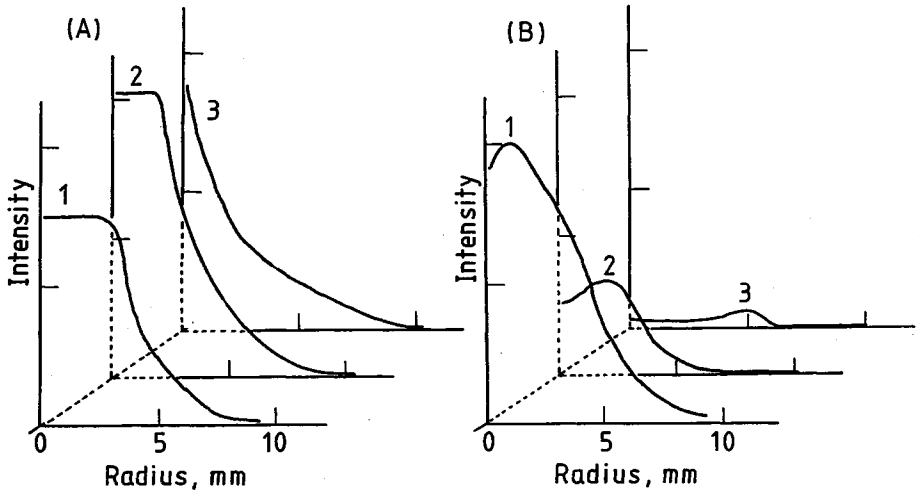

Figure 2. Radial Distribution of Emission Intensity at 247. 856 nm Atomic Carbon Line at Various Observation Height.

(A) Intensity of background carbon peak, (B) Intensity of net signal of carbon in sample. Observation height above load coil : 1, 5 mm ; 2, 15 mm ; 3, 25 mm.

2. These profiles were obtained by measuring the lateral distribution of the emission intensity at three observation heights, followed by the conversion to the radial distribution by the Abel inversion technique[10] assuming that a plasma flame is of circular symmetry. It is seen that the background emission spreads over the whole plasma flame, which corresponds to the visual emission region of it. The net signal by the analyte carbon is the largest near the center of the plasma flame at a observation height (OBH) of 5 mm, and is rapidly decreased and diffused to

the outside of the plasma with OBH increased, corresponding to the typical distribution of analyte emission[11]. These profiles strongly suggest that the background emission peak is due to the impurities of argon gas. Although it has been noticed that the emission from carbon appears on the background continuum of ICP, the origin of the carbon emission has been investigated in few reports[12),13)]. One of the reports[13)] asserts, on the fact that the emission from carbon was eliminated through the use of liquified source argon, that the source of carbon is oil in the compressed argon tank. The results obtained in this work support that assertion.

The background carbon emission was not reduced at all by passing argon gas through a column (35 mm i. d.×400 mm) packed with silica gel or molecular sieve (5A), or a gas trap bottle in which concentrated sodium hydroxide solution is filled. In addition, it was not reduced at all by use of compressed extra high purity argon (99.9995%) in a gas cylinder instead of the compressed high purity argon (99.998%).

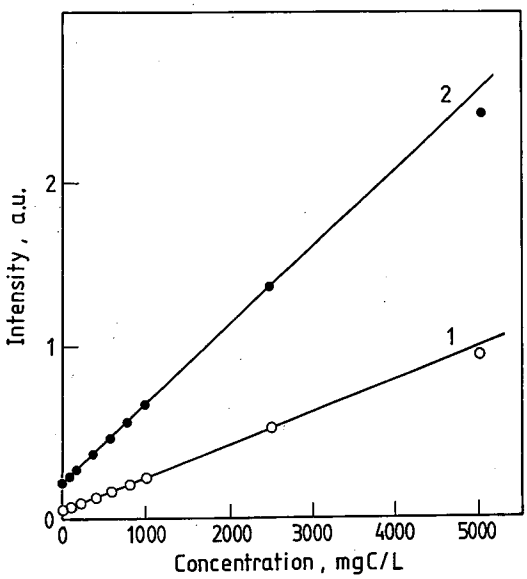

Figure 3. Calibration Curve of Carbon in Oxalic Acid.
1, 193.091 nm atomic line; 2, 247.856 nm atomic lime.

Dynamic Range and Detection Limit

Plot of the relative intensity versus the concentration of carbon is shown in Figure 3. The net intensity is linear to the concentration of carbon from 1 to 2500 mg/L over four orders of magnitude. The non-linearity at a concentration of 5000 mg/L is due to the decrease of the rate of sample introduction into plasma caused by increased viscosity of the sample solution[14)].

Table 2 shows the detection limit (DL), the background equivalent concentration (BEC), and the coefficient of variation (CV) for three atomic carbon lines[9)] under the optimized conditions listed in Table 1. DL and BEC are defined as the analyte concentration required to yield a net signal equivalent to three times the standard deviation of the background emission and that equivalent to background emission, respectively. The emission at 199.362 nm was so weak that it

Table 2. Analytical Line, Detection Limit (DL), Background Equivalent Concentration (BEC), and Coefficient of Variation (CV)

Line, nm	DL, mg/L	BEC, mg/L	CV, %*
C I 193.091	4.4	229	0.64
C I 199.362	-	-	-
C I 247.856	1.6	436	0.60

* Concentration of carbon is 500 mg/L. Ten measurements.
- Not detected.

was not detected with the ICP system used in this work. BEC for carbon is about three orders of magnitude larger than that for most of metallic elements (sub microgram-per-litter level). The larger BEC caused by the background carbon emission is one of the factors to give the poor detection limit, because detection limit is roughly proportional to BEC for ICP-AES[9]. Since the overall background emission intensity is about five and two times as large as the background cotinuum intensity at 193.091 nm and 247.856 nm, respectively, it is expected that the detection limit at those wavelengths is improved to be about 0.9 mg/L and 0.8 mg/L, respectively, if the impurities in the argon gas are completely removed.

Effect of Chemical Form of Carbon

Table 3 shows the relative intensity of the net signal obtained by aspirating aqueous samples containing some nonvolatile carbon compounds. These results indicate that carbon in nonvolatile compounds in aqueous samples yields almost the same response. The response, however, increased when aqueous ethanol solution was aspirated. Figure 4 shows the response curves of the emission intensity of carbon in oxalic acid and in ethanol when an aqueous solution of each compound was aspirated. The sensitivity for ethanol was measured to be

Table 3. Relative Response Factors of Various Compounds at the 247.856 nm Atomic Carbon Line

Compound	Empirical Formula	Response Factor*
Oxalic acid	$C_2H_2O_4$	(100)
Sodium carbonate	Na_2CO_3	100
EDTA	$C_{10}H_{16}O_8N_2$	100
Benzoic Acid	$C_7H_6O_2$	100
Starch	$(C_6H_{11}O_5)_n$	99

* The response for carbon of oxalic acid is defined as 100.
Concentration of each compound is 100 mg/L as carbon.

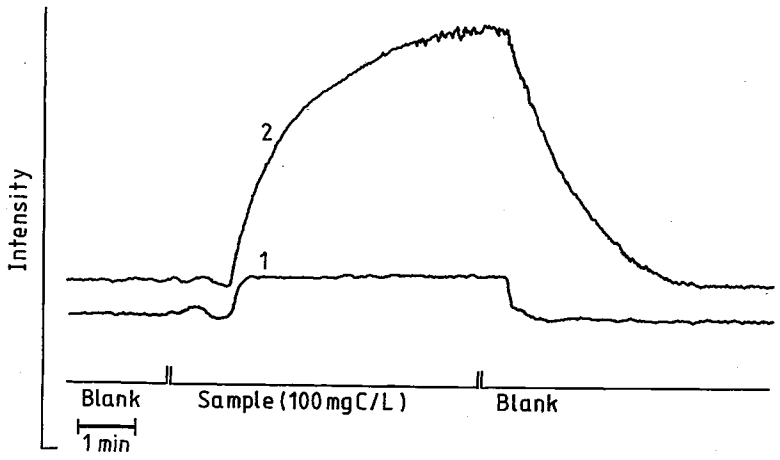

Figure 4. Signal Response at 247.856 nm by the Aspiration of Aqueous Samples.
1, Oxalic acid (100 mg C/L); 2, Ethanol (100 mg C/L).

about six times as large as that for oxalic acid. Similar response curves were obtained in the case of acetone and methanol. These results suggest that the increased sensitivity is common in volatile compounds. In addition, the response curves indicate that the time taken from the start of aspiration to the attainment of steady intensity with such compounds is longer than that with nonvolatile ones. The explanation is as follows : diminished pressure at nebulization and increased surface area of the aqueous phase by nebulization of sample solution enhance the volatilization of compounds in the nebulization chamber and the gaseous compounds are carried to plasma torch on argon gas flow together with the compounds in the aerosol. Thus, the enhancement of the sensitivity is attributable to the improvement of introduction efficiency of the analyte into plasma. The same kind of the enhancement in the sensitivity has been reported for ruthenium[15], osmium[16], silicon[17], gallium[18] and germanium[4]. Since the volatility of carbon compounds cannot be controlled with simple procedures such as the addition of a certain reagent into sample solutions, the enhancement effect caused by volatile compounds may be a serious problem in the determination of TC in aqueous samples.

Application to the Determination of Total Carbon in Waste Water

In general, TC in environmental aqueous samples including waste water is determined by the rapid combustion-infrared red absorption method (RC-IRA)[19]. In this method, some compounds which are difficult to decompose to carbon dioxide may not be measured without special care to the analytical condition such as an oxidation catalyst[20]. In comparison with this method, ICP-AES has the advantage that TC can be determined regardless of their chemical form and that carbon can be determined together with other elements at one measurement, although it requires a sample of relatively large volume (a few milliliters), it may suffer from the high detection limit, and samples containing volatile carbon compounds may yield inaccurate concentration data. Table 4 shows the concentration of TC in some samples determined by ICP-AES and RC-IRA. These samples were obtained at the drainageway from the kitchen, and they may contain carbon compounds such as fats, saccharides, proteins, and surfactants. The values obtained by ICP-AES are about ten times as large as those by RC-IRA. These differences are attributable to the existence of volatile carbon compounds or ones difficult to decompose. When monitoring the change of the carbon emission with time, it was found that the response for the waste water is similar to that for aqueous samples containing volatile carbon compounds such as ethanol shown in Figure 4. From this observation result, the main cause of the differences shown in Table 4 is probably volatile compounds dissolved in these samples. Since the enhancement factor for these samples (7.4～11.9) is larger than that for ethanol (6), the difference may be partly due to the compounds difficult to decompose in the procedure for RC-IRA method.

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Table 4. Total carbon in Waste Water from Kitchen Determined by ICP-AES and Rapid Combustion-Infrared Red Absorption Method (RC-IRA)

	Total Carbon, mg/L	
Sample No.	ICP-AES	RC-IRA
1	701	67
2	12	< 5
3	190	16
4	378	51
5	791	70

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